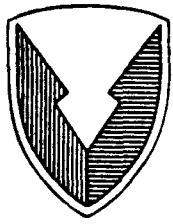


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Research and Development Technical Report
SLCET-TR-92-4

**First Year Testing of Prototype Magnesium/Manganese
Dioxide BA-4590/U Battery**

Louis Jarvis
Electronics Technology and Devices Laboratory

June 1992



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13. ABSTRACT (Maximum 200 words) A prototype magnesium/manganese dioxide battery, the BA-4590/U, was developed as a training battery replacement for the costly lithium BA-5590/U. At room temperature (21.1 deg C) the magnesium battery is cost-effective at 1.50 amperes and below. During continuous usage, delivered capacity of the lithium BA-5590/U exceeded that of the magnesium battery by at least 62 percent. Under SINGARS radio simulation testing, delivered capacity of the lithium battery exceeded that of the magnesium battery by at least 300 percent.				
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INTRODUCTION

In 1989 Rayovac Corporation, Madison, WI, was awarded a two year contract to develop an improved magnesium/manganese dioxide (magnesium) battery, the BA-4590/U. The contract number is DAAL01-89-C-0921. The battery must be identical in form, fit, and function to the lithium/sulfur dioxide battery (BA-5590/U) as described in MIL-B-49430(ER). Fifty BA-4590/U sample batteries were delivered to this laboratory after the first twelve months of the contract. These fifty batteries incorporate the various battery improvements made during the first year of effort. This report deals with the in-house government testing of the fifty deliverables.

PREVIOUS INVESTIGATIONS

During the Vietnam War magnesium batteries replaced LeClanche batteries because they possess enhanced elevated temperature storage and provide double the capacity [1]. Later works [2,3] in 1973 investigated various electrolyte-corrosion inhibitor systems directed at improving the shelf-life of partially discharged magnesium batteries by reducing the anodic corrosion. Until now, limited efforts have been pursued to improve the performance of the magnesium battery.

Faced with budget cuts, the U.S. Army is interested in reducing battery training costs. The projected low unit cost of the magnesium chemistry makes the prototype BA-4590/U an attractive candidate as a cost-effective training battery replacement for the BA-5590/U lithium battery. Shortcomings inherent with the standard magnesium electrochemical system, however, have made this replacement unrealistic. The contract, awarded to Rayovac, focusses on decreasing or eliminating the following inherent deficiencies: (1) excessive self discharge during storage following partial usage, (2) low discharge rate capability, (3) limited performance at reduced temperature (4.4°C and below), (4) dimensional distortion during discharge, and (5) excessive voltage delay at low temperature (4.4°C).

APPROACH

Tests were performed to characterize the following parameters of the prototype magnesium BA-4590/U battery: (1) weight, (2) dimensions, and (3) performance with respect to discharge temperature, discharge rate, intermittent storage, and simulated SINCGARS radio operation. BA-4590/U battery performance was compared to that of the lithium BA-5590/U under identical conditions. Finally, based on test results, a battery cost analysis was performed.

The magnesium battery consists of two 13.5-volt electrical sections. Each portion consists of 7 cells connected in series.

A 2.25-ampere slow-blow electrical fuse is incorporated within each section. The battery can be utilized with the sections connected in either a series or parallel arrangement. Nominal voltage is either 13.5 volts (parallel) or 27.0 volts (series).

As noted above the battery consists of 14 cells. The cells are designated 1601M-HR. The cell, cylindrical in shape, is 101.97 mm in height and 21.38 mm in outside diameter. The cells are of the bobbin construction. The anode, the can itself, is a magnesium alloy (AZ21). This is the same anode material utilized in the Rayovac production magnesium battery, the BA-4386/U. The alloy consists of magnesium (96.65%), aluminum (2.0%), zinc (1.0%), and minute quantities of manganese (0.2%) and calcium (0.15%). The cathode consists of an extruded mixture of manganese dioxide, Shawinigan acetylene black carbon, magnesium hydroxide (a pH buffer), and barium chromate (a corrosion inhibitor). The electrolyte is 3.5 N magnesium perchlorate with lithium chromate. The lithium chromate is also utilized for corrosion inhibition. The separator is an absorbent Kraft paper. The cell seal is a mechanical vent: a small hole in the top plastic washer that deforms under a certain amount of internal pressure. The vent allows the escape of hydrogen gas while minimizing water loss via evaporation.

EXPERIMENTAL PROCEDURE

Prior to discharge, dimensions and weight of all batteries were measured. Following discharge, battery dimensions were measured and compared to initial values. Dimensions prior to and following testing were compared to BA-5590/U dimensions as specified in MIL-B-49430(ER).

Electrical testing consisted of continuous constant current discharge, intermittent discharge, and SINCGARS radio simulation. All testing and data acquisition were performed on a 16-channel Techware Automated Battery Cycler. Potential vs time discharge data was stored on 5.25-inch floppy disks. A Tenny Jr temperature chamber was employed to maintain the battery environment at the appropriate temperature.

a. Continuous Discharge: Continuous constant current discharge was performed at 4.4, 21.1, and 43.3°C. Batteries were soaked for 8 hours at the appropriate temperature prior to discharge. The discharge rate varied from 100-3000 mA. Throughout testing internal and battery skin temperatures were recorded. The discharge time to 20.0 volts was used to calculate capacity.

b. Intermittent Discharge: Testing was performed at 500 mA and 21.1°C. Initially, batteries were partially discharged for one or three hours. The batteries were then stored at 21.1°C for one or four weeks. Discharge at 500 mA and 21.1°C was then

continued to an endpoint of 5.0 volts. The time to 20.0 volts was used for calculation of capacity. Battery performance was compared to that obtained for continuous discharge at 500 mA and 21.1°C.

c. SINGARS Simulation: Testing simulated typical usage of the SINGARS radio. The radio, which operates at constant power, is powered by one BA-5590/U battery in the 15 volt (parallel) mode. The discharge scenario consisted of 1 minute at 26.4 watts (transmit) followed by 9 minutes at 3.6 watts (receive). This cyclic regime was continued to a battery potential of 5 volts under the transmit mode. Testing was performed at -17.8, 4.4, 21.1, 43.3, and 71.1°C. Prior to discharge, all batteries were soaked at the appropriate temperature for 8 hours. The time to 10.0 volts was used for calculation of useful capacity.

DISCUSSION OF RESULTS

a. Weight and Dimensions: As noted in the lithium BA-5590/U specification, MIL-B-49430(ER), battery weight and dimension tolerances are as follows:

maximum weight:	1058 grams
height:	125.40 to 127.00 mm
length:	110.16 to 111.76 mm
width:	60.63 to 62.23 mm

All magnesium BA-4590/U batteries were within the weight specification (Table 1).

Prior to testing, the dimensions of three of the fifty batteries exceeded the specifications (Table 1). Following discharge the dimensions of thirty-three of the fifty BA-4590/U batteries exceeded battery specifications (Table 2). Continuous discharge resulted in greater dimensional increases than intermittent or SINGARS simulation. Battery expansion was a direct result of the individual cells swelling. The formation of magnesium hydroxide $Mg(OH)_2$ between the anode and cathode exerted internal pressure on the anode (can). This caused the individual cells to swell and crack open. This change in dimensions could result in difficulty in removing used batteries from equipment battery boxes.

b. Continuous Discharge: The effects of discharge conditions (rate and temperature) on BA-4590/U continuous discharge performance are shown in Figure 1 and Table 3. Delivered capacity is highly dependent upon discharge rate and temperature. Table 3 also shows that the magnesium BA-4590/U runs hot. As test conditions (discharge rate and ambient temperature) increased, the internal battery operating temperature also increased. This inherent characteristic of the magnesium system is beneficial at cold temperatures. The heat

generated at low discharge temperatures warms the battery and improves performance. At elevated conditions (discharge rates and temperature) this additional heat could pose a handling problem. The maximum recorded skin temperature of batteries 15 through 30 (Table 3) exceeded 45°C, which is the pain threshold for skin [4].

Regression analysis [5] was utilized to develop best fit equations of the test data. Figure 2 compares the actual test data to the curves obtained from regression analysis (predicted data). At every discharge temperature (4.4, 21.1, and 43.3°C), the predicted data curve correlates well with the test data. Table 4 shows that the percent deviation is greater than 14% only at 2.0 amperes and temperatures above 43.3°C. Throughout the remaining test conditions, the maximum deviation is 8.4%.

Figure 3 compares the continuous discharge performance of the magnesium BA-4590/U with the lithium BA-5590/U. Unlike the magnesium battery, lithium battery performance is highly stable throughout the various discharge conditions. Lithium BA-5590/U capacity exceeded that of the magnesium BA-4590/U by more than 60%.

c. Intermittent Discharge: Partially used magnesium batteries do not store well as a result of anode corrosion. Figure 4 and Table 5 show the effect of this intermittent usage on the BA4590/U battery. Figure 4 also shows that for the full impact of the intermittent usage, more than 15% of the available capacity must initially be removed. This amount of initial discharge fully exposes the anode surface to electrolyte by totally removing the protective magnesium hydroxide film. Once removed, the film does not reform to its original degree of protection thus allowing rapid anode corrosion.

The slopes of the lines in Figure 4 were obtained by linear regression and represent the effective service hours lost per day as a result of the anode corrosion that occurs during storage following initial partial usage. The ratio of the two slopes is 5.64. Compared to initially removing 15% of the available capacity, self discharge rates are over 4 times higher when 45% of the capacity is initially removed.

d. SINCGARS Performance Simulation: The effect of SINCGARS testing on BA-4590/U is shown in Figure 5 and Table 6. As in continuous discharge, battery performance is highly dependent upon temperature. Figure 6 compares the SINCGARS simulation performance of the magnesium BA-4590/U against that of the lithium BA-5590/U. Lithium battery operation is at least 3 times greater at all conditions.

e. Cost Analysis: A battery usage comparison of the prototype magnesium BA-4590/U versus the lithium BA-5590/U was

performed. Battery operating costs for continuous discharge and SINCGARS simulation were investigated. The analysis is based on the following:

- 1) one day (24 hrs) of usage
- 2) Battery unit costs:
 - lithium BA-5590/U: \$45.00
 - magnesium BA-4590/U: \$13.50

Figures 7, 8, and 9 compare continuous discharge operating costs. At 4.4°C (Figure 7) the magnesium BA-4590/U battery is cost effective at rates of 250 mA and below. Above 250 mA, the magnesium battery is more expensive to operate. This is due to the reduced performance at the higher discharge rates (Table 3). At 21.1°C (Figure 8) magnesium battery usage is cost effective at 1.5 amperes and below. At 43.3°C (Figure 9), the magnesium battery is cost effective at 2.0 amperes and below. At 43.3°C, note the excessive magnesium operating cost at 2.5 amperes. For twenty-four hours of usage, magnesium battery operating costs are \$6,480 versus \$403 for lithium.

Figure 10 compares SINCGARS battery operating costs. Cost savings via magnesium battery usage are realized only at 71.1°C and above. At room temperature (21.1°C) magnesium BA-4590/U operating cost is more than 4 times greater than that of the lithium BA-5590/U.

The above cost analysis assumes battery usage on a continuous basis. The test data (Table 4 and Figure 4) show that intermittent use of the BA-4590/U would reduce the cost effectiveness of the magnesium battery as a consequence of the self discharge phenomenon.

CONCLUSIONS

1. Continuous Discharge:

a. Unlike the lithium BA-5590/U, delivered capacity of the magnesium BA-4590/U battery is highly dependent upon both the discharge rate and temperature.

b. Delivered capacity of the magnesium BA-4590/U battery increases with reduced discharge rates and higher temperature.

2. Intermittent Discharge:

a. Unlike the lithium BA-5590/U battery, the magnesium BA-4590/U loses capacity (self discharge) during idle storage after initial usage.

3. SINCGARS Simulation:

a. Unlike the lithium BA-5590/U, delivered capacity of the magnesium BA-4590/U is highly dependent upon the discharge temperature.

b. Compared to the BA-4590/U, delivered capacity of the lithium BA-5590/U is at least three times greater at all conditions.

4. Weight and Dimensions:

a. Weights of all 50 BA-4590/U batteries were within the MIL-B-49430(ER) specification.

b. Following discharge, dimensions of 32 BA-4590/U batteries increased. This resulted in 66% of the batteries exceeding dimensional specifications.

5. Operating Costs:

a. Continuous discharge cost effectiveness of the BA-4590/U is highly dependent upon discharge conditions (rate and temperature), as follows:

BA-4590/U Cost Effective Conditions

Temperature (°C)	Discharge Rate (A)
4.4	≤ 0.25
21.1	≤ 1.50
43.3	≤ 2.00

b. Under SINCGARS simulation, the BA-4590/U is cost effective at temperatures of 71.1°C and above.

FUTURE PLANS

1. Field test comparison of magnesium BA-4590/U vs lithium BA-5590/U.

2. In-house "bench" testing using actual end-item communications equipment.

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TABLE 1. BA-4590/U Weights and Initial Dimensions

Battery Number	Weight (g)	Average Initial Dimensions (mm)		
		Height	Length	Width
1	975	126.31	110.52	62.07
2	984	126.60	110.57	*62.26
3	983	126.45	111.28	61.64
4	978	126.97	111.43	61.71
5	982	126.58	111.14	61.60
6	979	126.70	111.17	61.97
7	981	126.43	111.27	61.82
8	980	126.57	111.26	61.88
9	979	127.00	111.41	61.88
10	974	126.31	111.16	61.81
11	988	126.87	111.32	61.67
12	981	126.51	111.28	61.61
13	975	126.76	111.12	61.98
14	978	126.67	111.20	61.64
15	976	126.68	111.22	61.84
16	984	126.48	111.13	61.63
17	982	126.81	111.12	62.03
18	978	126.57	111.36	61.68
19	978	*127.16	110.93	61.82
20	978	126.80	111.10	61.99
21	980	126.63	111.35	61.54
22	987	126.61	111.12	61.57
23	979	126.83	111.12	61.88
24	983	126.48	111.47	61.62
25	977	126.46	111.03	61.83

TABLE 1. Continued

Battery Number	Weight (g)	Average Initial Dimensions (mm)		
		Height	Length	Width
26	983	126.49	111.24	61.71
27	981	126.72	111.14	61.25
28	976	126.49	110.96	61.73
29	975	126.32	111.06	61.79
30	976	126.52	111.03	61.57
31	976	126.40	111.27	61.58
32	976	126.65	110.62	61.83
33	981	126.08	111.20	61.70
34	974	126.49	111.95	61.77
35	976	125.93	110.98	61.64
36	976	126.30	110.73	61.87
37	995	126.66	110.68	61.88
38	979	126.53	110.87	61.76
39	974	126.40	110.40	61.98
40	979	125.62	110.53	61.48
41	972	125.84	110.74	61.72
42	977	126.11	110.91	61.59
43	970	126.06	111.18	61.49
44	985	127.18	110.77	61.57
45	974	125.92	111.77	61.76
46	978	126.16	110.80	61.59
47	971	125.57	110.73	61.87
48	988	125.50	110.56	61.79
49	971	*125.27	110.43	61.71
50	978	126.22	110.87	61.74

* Dimension is not within BA-5590/U specification

TABLE 2. BA-4590/U Dimensions Following Discharge

Battery Number	Average Final Dimensions (mm)		
	Height	Length	Width
1	126.73	111.39	*62.45
2	*127.38	111.04	62.15
3	*127.49	*112.61	*62.51
4	*128.10	*113.13	*62.71
5	126.53	110.91	61.93
6	*126.16	111.07	61.69
7	*127.52	111.28	61.68
8	*127.16	111.23	61.68
9	*128.29	*113.71	*61.94
10	126.66	111.03	61.84
11	*127.42	111.48	61.84
12	*127.66	111.55	61.79
13	*127.07	111.09	62.26
14	*127.70	111.32	*62.44
15	*127.61	110.93	*62.33
16	*127.13	111.09	*62.33
17	*128.43	*112.59	*62.97
18	*128.36	*112.25	*62.50
19	*127.12	111.56	62.19
20	*127.24	*112.30	*63.01
21	*127.54	*112.46	*63.95
22	*128.73	*113.97	*62.93
23	*128.82	*114.11	*63.44
24	126.43	111.31	61.73
25	126.81	111.43	61.88

TABLE 2. Continued

Battery Number	Average Final Dimensions (mm)		
	Height	Length	Width
26	*128.22	*112.49	*62.32
27	*129.33	*112.76	*62.68
28	*127.76	*111.84	*62.66
29	*127.73	111.57	*62.43
30	*127.68	111.68	*62.50
31	126.85	111.53	*62.48
32	126.17	110.74	61.87
33	125.74	111.33	61.80
34	126.13	110.78	61.64
35	125.68	111.12	61.58
36	125.86	111.29	61.64
37	125.92	111.32	61.83
38	125.87	111.17	61.81
39	126.10	111.15	62.07
40	125.59	110.64	61.66
41	125.78	110.83	61.70
42	126.07	110.78	61.46
43	125.82	111.02	61.63
44	125.66	111.17	61.86
45	125.49	*111.86	62.06
46	125.61	111.73	62.10
47	126.11	*112.51	61.99
48	125.99	*112.50	61.76
49	126.02	*112.09	61.88
50	126.42	*112.02	61.70

* Dimension is not within BA-5590/U specification

TABLE 3. Continuous Discharge Effects of Discharge Rate and Temperature on BA-4590/U Performance

Battery Number	Discharge Conditions		Service to 20 Volts (Hr)	Capacity (A-Hr)	Battery Temp	
	Rate (A)	Temperature (°C)			Internal (°C)	Skin (°C)
5	.10	4.4	31.50	3.15	not recorded	not recorded
6	.25	4.4	9.77	2.44	50	11
7	.50	4.4	4.05	2.03	52	16
8	.75	4.4	2.18	1.64	67	18
9	.10	21.1	44.5	4.45	not recorded	22
10	.25	21.1	14.72	3.68	45	24
11	.50	21.1	6.58	3.29	61	28
12	.50	21.1	6.70	3.35	59	27
13	1.00	21.1	2.57	2.57	85	33
14	1.00	21.1	3.05	3.05	77	28
15	1.50	21.1	1.35	2.03	107	51
16	1.50	21.1	1.68	2.52	110	49
17	2.00	21.1	1.00	2.00	121	46
18	2.00	21.1	1.00	2.00	123	46
19	0.50	43.3	8.57	4.29	79	48
20	1.00	43.3	3.48	3.48	104	51
21	1.00	43.3	3.58	3.58	not recorded	53
22	1.50	43.3	1.93	2.90	129	69
23	1.50	43.3	1.92	2.88	129	71
28	2.00	43.3	1.08	2.16	148	57
29	2.00	43.3	1.10	2.20	156	61
30	2.50	43.3	0.05	0.13	162	66

TABLE 4. BA-4590/U Continuous Discharge Comparison
of Experimental versus Predicted Performance

Discharge Temp (°C)	Discharge Rate (A)	Capacity (A-Hr)		Percent Deviation (%)
		Experimental	Predicted	
4.4	.10	3.2	3.0	3.1
4.4	.25	2.4	2.6	7.7
4.4	.50	2.0	2.0	0.0
4.4	.75	1.6	1.6	0.0
21.1	.10	4.4	4.0	10.0
21.1	.25	3.7	3.8	2.7
21.1	.50	3.3	3.5	6.1
21.1	1.00	2.8	2.9	3.6
21.1	1.50	2.3	2.3	0.0
21.1	2.00	2.0	1.9	5.0
43.3	.50	4.3	4.0	-7.5
43.3	1.00	3.5	3.8	8.6
43.3	1.50	2.9	3.1	6.9
43.3	2.00	2.2	1.9	13.6
43.3	2.50	0.1	0.2	100.0

TABLE 5. BA-4590/U Effect of Intermittent Discharge

Discharge Rate: 0.50 A
 Discharge Temperature: 21.1°C

Battery Number	Initial Service Removed		Storage Period (Day)	Service Following Storage (Hr)	Total Service to 20 Volts (Hr)	Service Lost		Average Service Lost (Hr)
	HR	(%)				(Hr)	(%)	
1	1.00	15	28	5.68	6.68	0.00	0.0	.42
2	1.00	15	28	4.80	5.80	0.84	12.7	
24	1.00	15	12	5.43	5.43	0.21	3.2	.35
25	1.00	15	12	5.15	5.15	0.49	7.4	
3	3.00	45	28	1.40	4.40	2.24	33.7	2.23
4	3.00	45	28	1.42	4.42	2.22	33.4	
26	3.00	45	12	2.52	5.52	1.12	16.9	1.18
27	3.00	45	12	2.40	5.40	1.24	18.7	

TABLE 6. SINGARS Simulation. Temperature Effects
on BA-4590/U Performance

Battery Number	Discharge Temperature (°C)	Service to 15 Volts (Hr)	Average Service (Hr)
49	-17.8	0.00	0.00
50	-17.8	0.00	
36	4.4	0.65	1.06
37	4.4	1.67	
38	4.4	0.50	
39	4.4	1.83	
47	4.4	0.84	
48	4.4	0.84	
32	21.1	2.33	2.30
33	21.1	2.35	
34	21.1	2.33	
35	21.1	2.17	
40	43.3	4.00	5.63
41	43.3	8.02	
42	43.3	4.83	
43	43.3	5.68	
31	71.7	12.33	12.30
44	71.7	12.68	
45	71.7	12.17	
46	71.7	12.00	

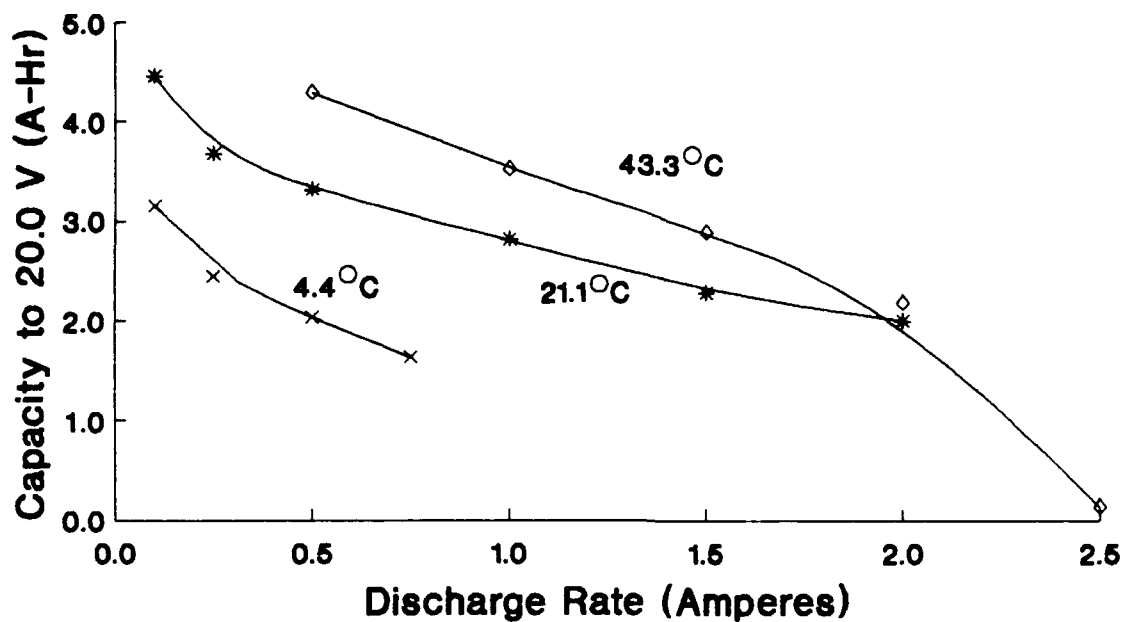


Figure 1. Continuous Discharge. Effect of rate and Temperature on BA-4590/U Performance.

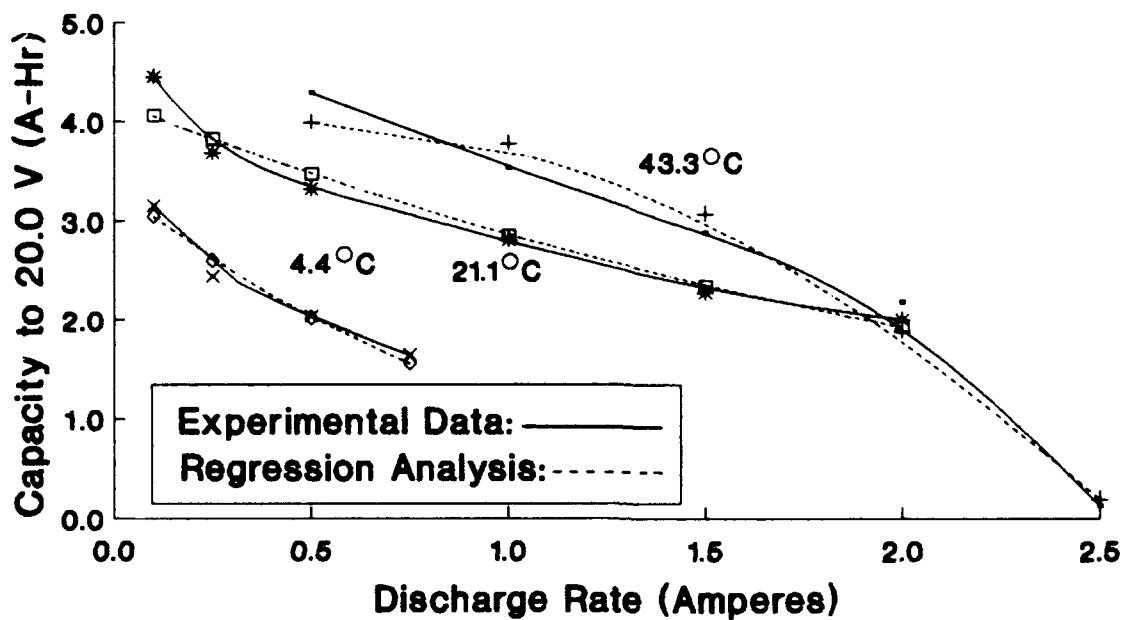


Figure 2. Regression Analysis of Continuous Discharge Experimental Data.

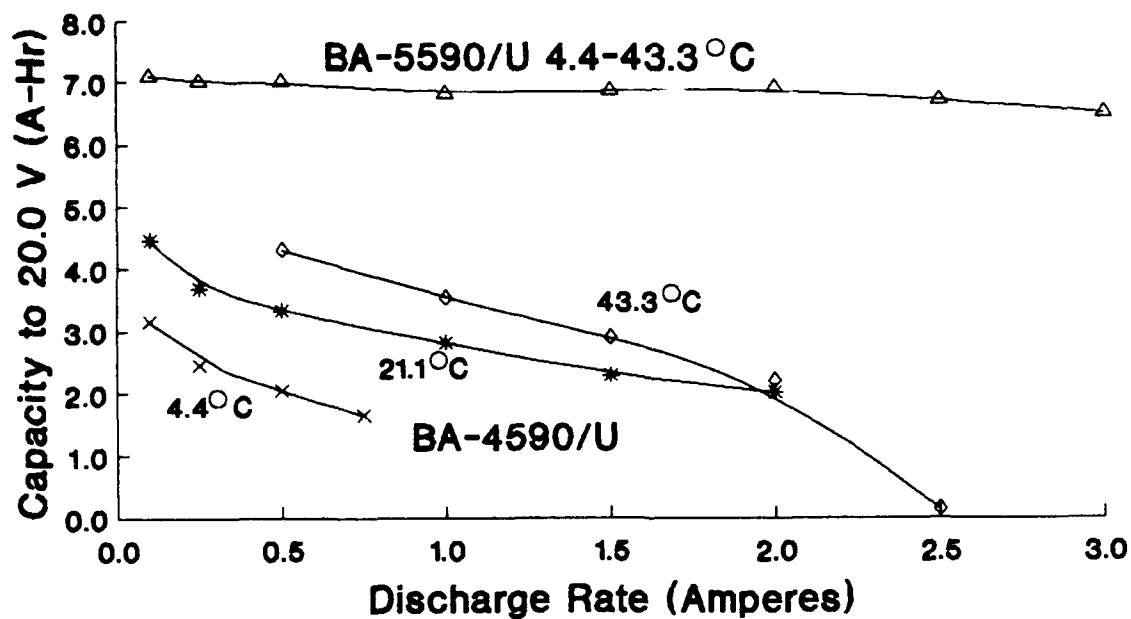


Figure 3. Continuous Discharge. Effect of Rate and Temperature on Battery Performance.

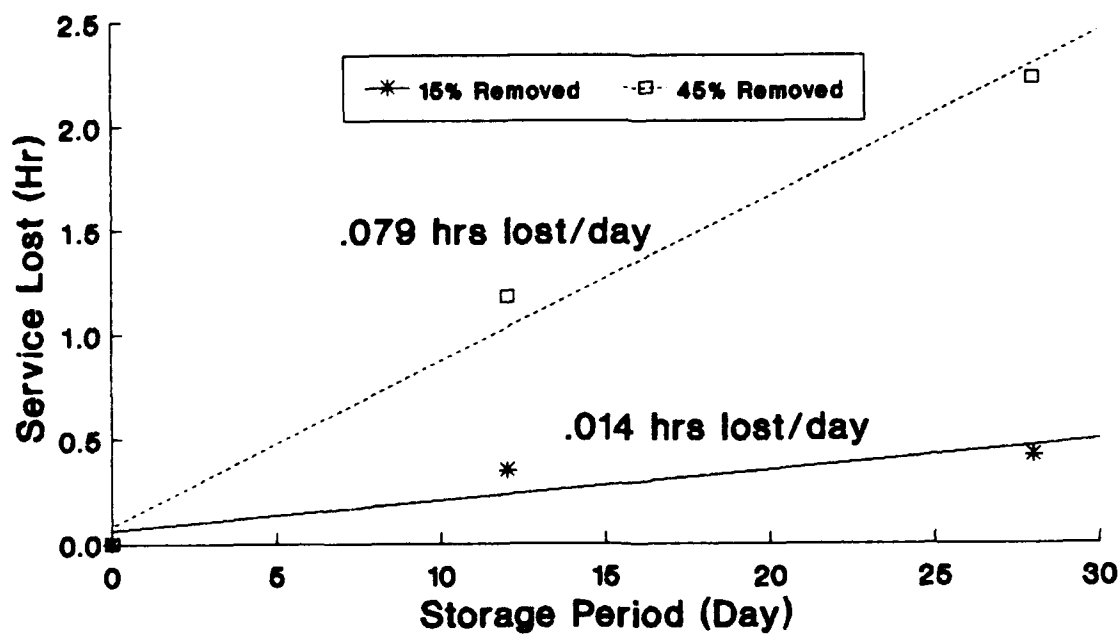


Figure 4. Effect of Intermittent Discharge on BA-4590/U Performance.

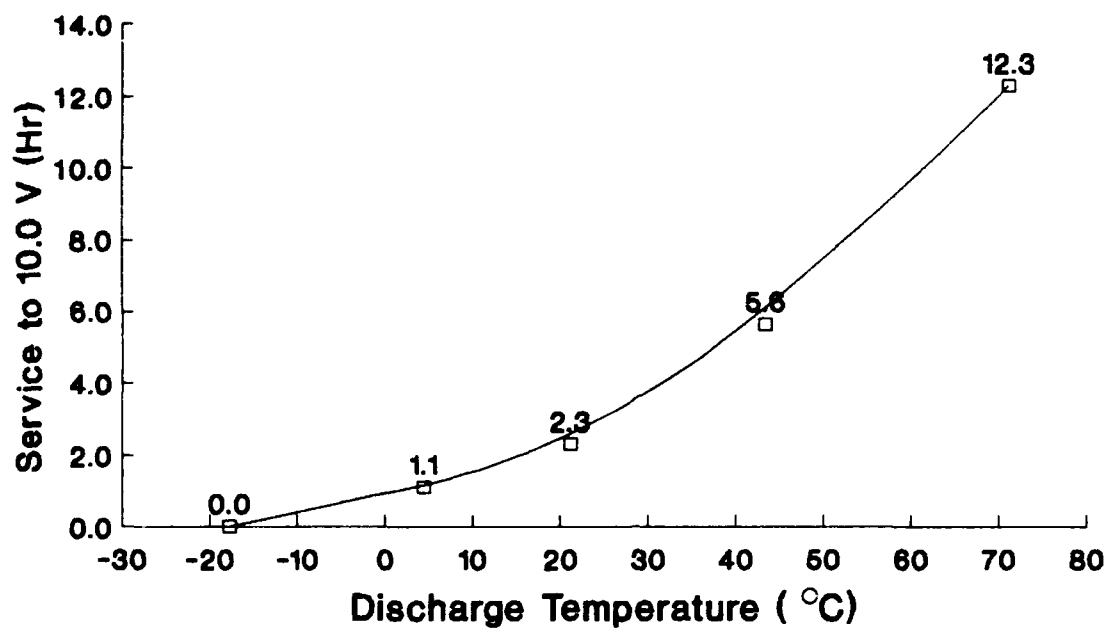


Figure 5. SINGARS Simulation. Effect of Temperature on BA-4590/U Performance.

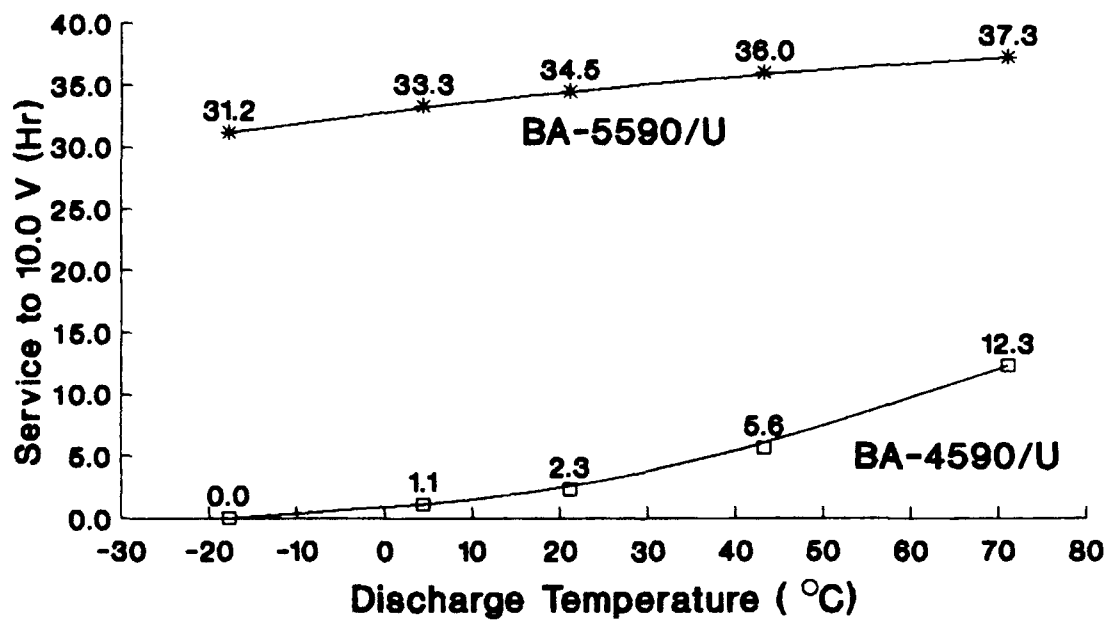
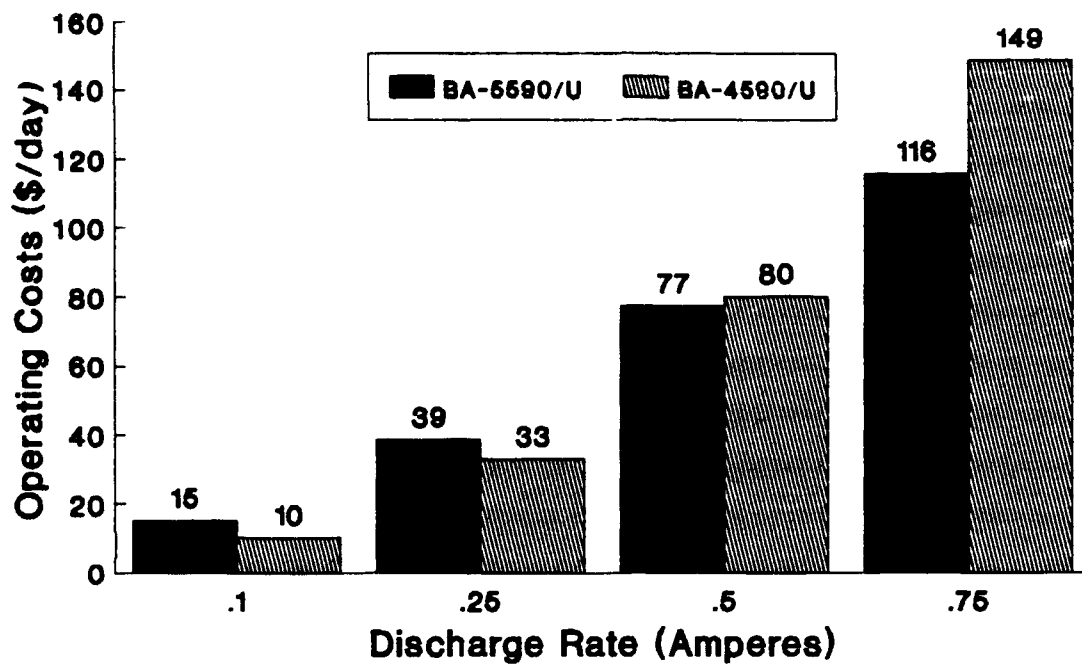
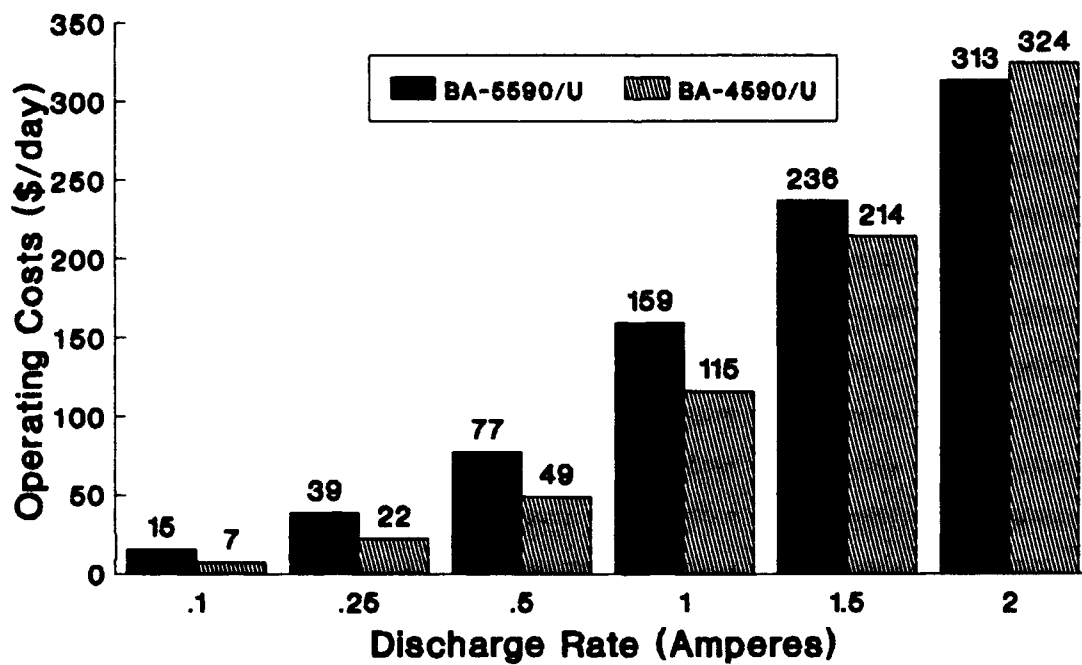


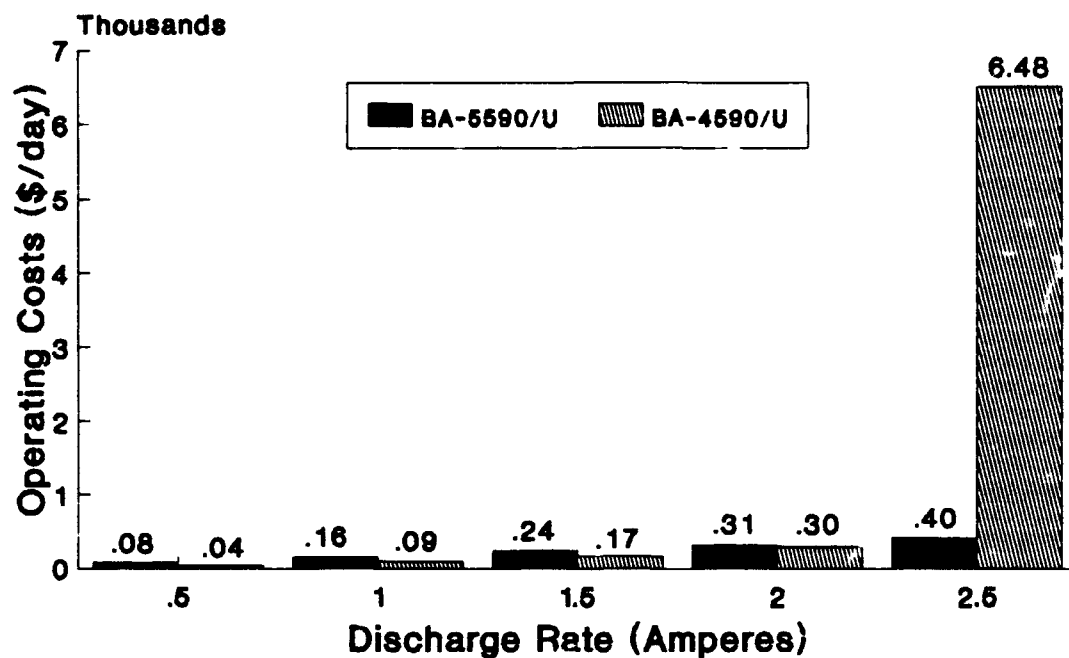
Figure 6. SINGARS Simulation. Effect of Temperature on Battery Performance.



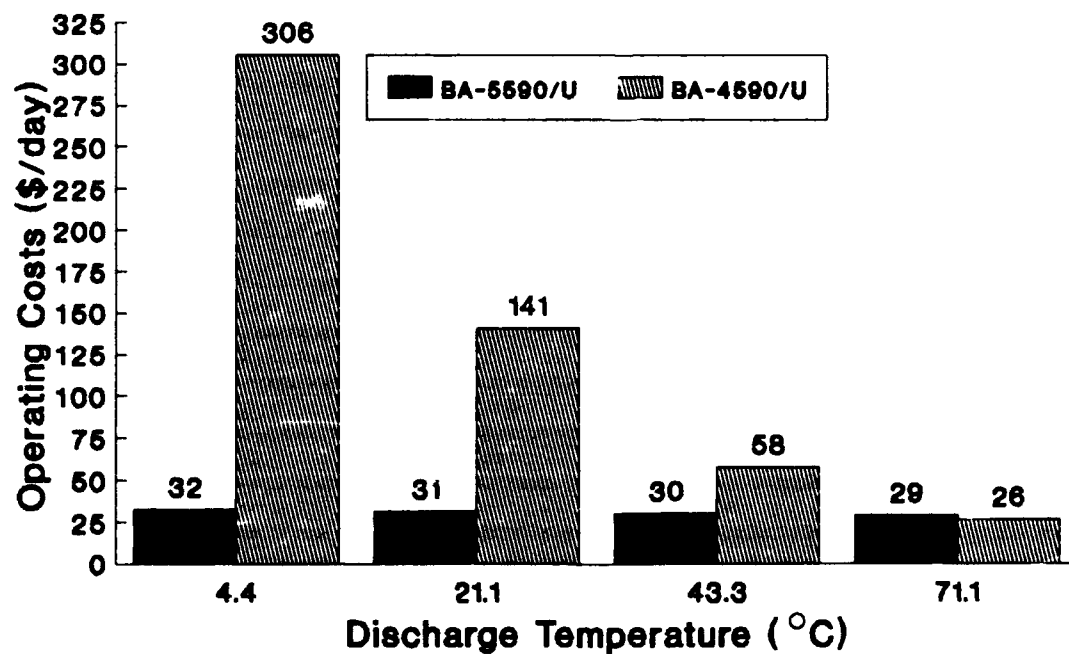
**Figure 7. Continuous Discharge.
Battery Operating Costs at 4.4°C.**



**Figure 8. Continuous Discharge.
Battery Operating Costs at 21.1°C.**



**Figure 9. Continuous Discharge.
Battery Operating Costs at 43.3°C**



**Figure 10. SINGARS Simulation.
Battery Operating Costs.**

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